

VLE measurements and correlation for the R125+R600 system¹

L. Fedele^{2,4}, S. Bobbo², R. Camporese² and R. Stryjek³

¹ Paper presented at the Fifteenth Symposium on Thermophysical Properties, June 22-28, 2003, Boulder, Colorado, U.S.A.

² National Research Council, Institute of Building Technologies – Division of Padova, Corso Stati Uniti, 4. I-35127 Padova, Italy.

³ Institute of Physical Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, 01-224 Warsaw, Poland.

⁴ To whom correspondence should be addressed (tel. +39 049 8295706, fax +39 049 8295728 and e-mail: laura.fedele@itc.cnr.it)

Abstract

Hydrocarbons and hydrofluorocarbons mixtures are amongst the possible substitutes of chlorinated refrigerants. This family of mixtures, as pointed out in our studies on VLLE for the R32 + R290 and R32 + R600 systems, shows the possibility of liquid phase splitting. In this work, the liquid immiscibility of the R125 + R600 system has been measured with the cloud point method down to 200 K in a sealed glass cell of about 30 cm³ and equipped with magnetic stirrers. The temperature is maintained at ± 3 mK and measured to within ± 0.1 K. Uncertainty in pressure is estimated to be within ± 4 kPa. The bulk composition is gravimetrically measured with an accuracy of ± 0.005 in mole fraction.

Having measured P - T - x data, the VLLE parameters are derived using the RKS and PR EoS, both with the Huron-Vidal mixing rule with the NRTL equation for the excess Gibbs free energy at infinite pressures.

KEYWORDS: experimental method, liquid-liquid equilibria, mutual solubility, mixture, pentafluoroethane (R125), *n*-butane (R600).

1. Introduction

In the attempt to determine suitable substitutes for the chlorinated refrigerants, particular attention has to be paid to mixtures composed by hydrocarbons and hydrofluorocarbons. Following our studies on vapour-liquid-liquid equilibria (VLLE) for the difluoromethane (R32) + propane (R290) [1] and R32 + *n*-butane (R600) [2] systems, the mutual solubility for the pentafluoroethane (R125) + R600 system is measured in this work. The second aim of our study is to develop a method for the VLLE parameter derivation with an EoS approach based on mutual solubility data.

The VLLE for the chosen system is of interest from both the theoretical and the practical point of view, because they provide new information that is important due to possible influence on the operation of refrigerating machines.

2. Experimental

Materials. R125 (pentafluoroethane, C₂HF₅) was provided by Solvay, with a declared purity > 99.9% and R600 (*n*-butane, C₄H₁₀) by Aldrich with a stated purity > 99%. After the elimination of the non-condensable gases, no impurities were identified by gas-chromatographic analyses performed with both thermal conductivity (TCD) and flame ionisation (FID) detectors; a Porapak Q column with a length of 2 m and an external diameter of 1/8'' was used. All samples were used with no further purification.

Apparatus. The set-up used in the present work has already been described in detail [1, 2] and used without modification, so only essential information is reported here. The measurements were taken in a sealed glass cell with a volume of about 30 cm³. The glass cell was equipped with internal magnetic stirrers. It was immersed in an ethyl alcohol bath of about 2.5 L capacity. The temperature of the set-up was maintained at ± 5 mK by means of a PID-controlled system. Low temperatures were reached by means of an auxiliary refrigerator (Lauda RUK 90). Temperature was measured with a 100 Ω platinum resistance thermometer. Pressure was measured by a differential pressure gauge (Druck DPI 145) with a full scale of 70 bar. The bulk composition was

gravimetrically measured with an uncertainty of ± 0.005 in mole fraction and it was taken as corresponding to the liquid composition at the cloud point.

Measurements. Liquid phase split was visually observable from the appearance of the cloud point. The equilibrium temperature was measured with an uncertainty of ± 0.1 K. At the equilibrium temperature, the overall uncertainty in pressure measurements was estimated to be within ± 4 kPa.

3. Results and discussion

The appearance of the cloud point for this system was observed at temperatures below 216 K. Twenty four experimental P - T - x data for the R125 + R600 mixture covering both branches of the binodal boundary are given in Table 1 and plotted in Figure 1. Few data were measured in the vicinity of the upper critical solution (alternatively named consolute) temperature where a very strong opalescence was observed.

Binodal boundary representation. The LLE can be derived exploiting T - x solubility data provided only they are distributed along both branches of the binodal boundary. The composition of the second liquid phase can be estimated either graphically or numerically. In this study, three different methods were applied. The results are shown in Figure 1 and in Table 1.

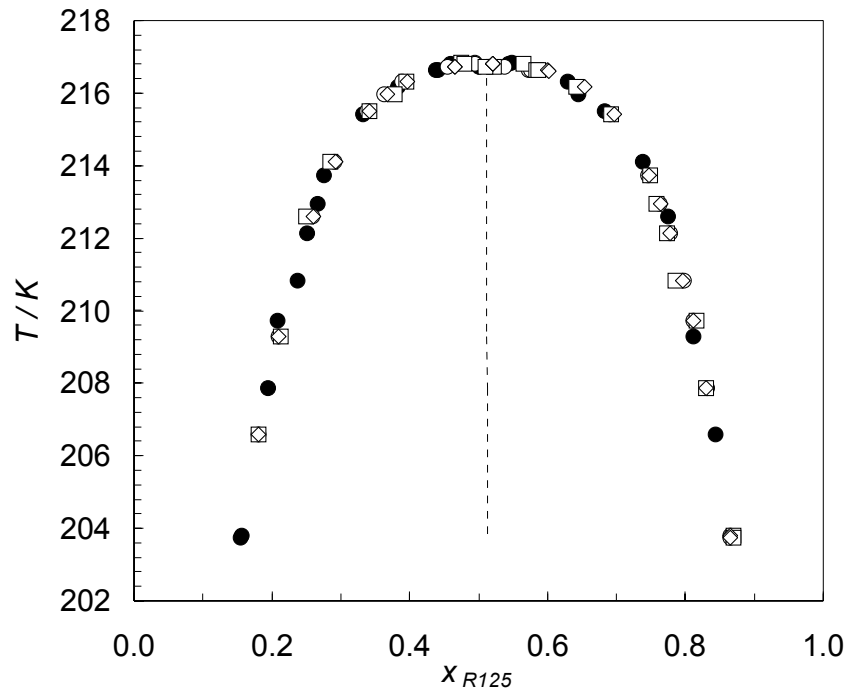


Figure 1. Mutual solubility data for the R125 + R600 system; experimental (●) and estimated liquid phase composition with the polynomial (○), the binodal method (□) and eq. (4) (◇). The dashed line (—) represents the rectilinear diameter.

The first method is based on the regression of the T - x data forming the binodal boundary with a sixth degree polynomial. The results of the regression were used to calculate the second liquid phase composition coexisting in equilibrium at the experimental temperature. Optionally (not applied here) the composition of both liquid phases may be calculated from the regressed polynomial: in general, it gives smoother LLE phase compositions.

Table 1. Experimental cloud point data for the R125 + R600 system and estimated compositions with: 1 - polynomial, 2 - binodal, and 3 – equation (3).

Sample	<i>Experimental</i>			<i>Estimated</i>			
	x_{R125}^{L1}	$T_{\text{exp}} / \text{K}$	$P_{\text{exp}} / \text{kPa}$	1 $x_{\text{est-R125}}^{L2}$	2 $x_{\text{est-R125}}^{L2}$	3 $x_{\text{est-R125}}^{L1}$	3 $x_{\text{est-R125}}^{L2}$
1	0.1553	203.75	32.2	0.8658	0.8696	0.1549	0.8649
2	0.1556	203.79	31.5	0.8655	0.8693	0.1552	0.8646
3	0.1949	207.87	40.5	0.8314	0.8297	0.1930	0.8307
4	0.2088	209.73	45.7	0.8114	0.8157	0.2149	0.8109
5	0.2381	210.84	47.9	0.7972	0.7863	0.2301	0.7970
6	0.2514	212.13	52.0	0.7778	0.7729	0.2508	0.7781
7	0.2659	212.94	54.4	0.7631	0.7583	0.2661	0.7639
8	0.2755	213.73	55.0	0.7462	0.7487	0.2837	0.7476
9	0.3317	215.43	62.8	0.6909	0.6923	0.3388	0.6961
10	0.3827	216.17	64.5	0.6427	0.6413	0.3828	0.6542
11	0.4374	216.62	67.2	0.5763	0.5866	0.4373	0.6016
12	0.4407	216.63	66.1	0.5732	0.5833	0.4393	0.5996
13	0.4591	216.80	67.3	0.4947	0.5648	0.5200	0.5200
14	0.5012	216.73	68.4	0.5379	0.5228	0.5735	0.4659
15	0.5140	216.73	72.0	0.4547	0.5100	0.5735	0.4659
16	0.5440	216.80	66.5	0.4947	0.4799	0.5200	0.5200
17	0.5487	216.85	63.9	0.4947	0.4752	0.5200	0.5200
18	0.6294	216.32	63.7	0.3890	0.3946	0.6412	0.3963
19	0.6453	215.97	66.2	0.3626	0.3787	0.6682	0.3681
20	0.6830	215.49	61.5	0.3378	0.3410	0.6934	0.3415
21	0.7387	214.10	56.2	0.2915	0.2855	0.7388	0.2932
22	0.7752	212.61	54.2	0.2589	0.2490	0.7699	0.2596
23	0.8119	209.29	43.5	0.2095	0.2126	0.8159	0.2093
24	0.8443	206.60	37.7	0.1804	0.1804	0.8424	0.1801

The second method is based on the idea that the compositions of the two liquid phases in equilibrium should be well represented by the rectilinear diameter rule defined as:

$$x_{R125,rect} = \frac{(x_{R125}^{L_1} + x_{R125}^{L_2})}{2} \quad (1)$$

For the system, the rectilinear diameter shows only slight temperature dependence over the entire temperature range, excluding the region very close to the UCST, and it can be represented by the following expression:

$$x_{R125,rect} = -3.669247 \cdot 10^{-5} \cdot T/K + 5.199281 \cdot 10^{-1} \quad (2)$$

In Figure 1 the course of the rectilinear compositions is also shown.

In the third method the reduced critical solution temperature is represented by the following equation:

$$T_r = 1 + \sum_{k=1}^n A_k (2z_i - 1)^{2k} \quad (3)$$

as a function of the composition expressed as the z_i fraction, defined:

$$z_i = \frac{x_i}{x_i + x_j q_{ji}} \quad (4)$$

where $q_{ji} = q_j/q_i = x_j^{UCST}/x_i^{UCST}$. As pointed out by Rogalski and Stryjek [3], the binodal boundary expressed in the z_i fraction forms a universal and symmetric curve for various systems, even with components of large differences in liquid molar volumes. In equation 3, A_k are adjustable parameters and, in this work, only two A_k parameters were able to represent the binodal boundary provided the ratio q_j/q_i is also fitted in the regression procedure.

All these methods can accurately describe the binodal boundary and we found only small differences among them except a narrow temperature range in the proximity of the consolute temperature ($T_{UCST} - T < 0.1$ K) where the observed differences are greater.

Here some substantial differences should be mentioned between the first two and the third method of LLE derivation. In the first two methods, the corresponding liquid phase composition has been found in respect to the experimental temperature and the measured composition at the cloud point; on the contrary, using equation 4 with regressed coefficients A_k , the composition of both liquid phases has been calculated at the temperature of the cloud point.

The temperature $T = 216.8$ K and the composition $x_{R125} = 0.50$ of the upper critical solution point were estimated as the average of the results of the three different methods. The pressure of the consolute point $P = 67$ kPa was calculated by means of the Antoine equation as here below described.

Equilibrium temperature and pressure. Since we measured the system equilibrium pressure at the cloud points, the reduction of the T - P data combined in one set enables to evaluate the random errors for the measured quantities. We used the Antoine equation

$$\log(P / \text{kPa}) = A - \frac{B}{(T / K) + C} \quad (5)$$

The equation 5 gives an AAD of about 0.82 kPa. The found deviations are smaller than the estimated by us uncertainty in pressure measurements. The parameters of equation 5 are $A = 7.533972666$, $B = 1396.6819557$ and $C = 27.820274$.

The advantage of this method is that the data belonging to both branches of the binodal boundary, and even in the proximity of the UCST, are well represented by one

set of parameters.

Data correlation. The Φ - Φ approach has been applied to correlate the LLE and to derive the VLLE parameters. The measured T - P - x^{L1} along with the derived second liquid phase compositions x^{L2} were used to regress the parameters of the Redlich-Kwong-Soave (RKS) [4] and the Peng-Robinson (PR) [5] equations of state (EoS). In these equations:

$$a = \Omega_a \frac{(RT_c)^2}{P_c} \cdot \gamma(T) \quad (6)$$

and

$$b = \Omega_b \frac{(RT_c)}{P_c} \quad (7)$$

The temperature dependence of the γ parameter in the RKS and PR EoS was approximated by the following expression adopted from Zabaloy and Vera [6]:

$$\gamma = 1 + B_1 \cdot T_r \cdot \ln(T_r) + B_2 \cdot (T_r - 1) + B_3 \cdot (T_r^2 - 1) \quad (8)$$

where $T_r = T/T_c$. The B_i parameters are substance dependent coefficients regressed on the saturated pressures of the pure compounds and the critical parameters taken from the database REFPROP 7.0 [7]. All the involved parameters along with the found B_i coefficients are reported in Table 2. Both EoSs were used with the Huron-Vidal (HV) mixing rule [8] and the NRTL equation [9] to represent the excess Gibbs free energy at infinite pressures.

Table 2. Parameters of the RKS and PR EoSs.

	<i>RKS EoS</i>		<i>PR EoS</i>	
Ω_a	0.4274800		0.4572355	
Ω_b	0.0866403		0.0777960	
	R125	R600	R125	R600
B_1	3.8424563973	2.4519198385	3.1481091549	2.0222478248
B_2	-1.1424396280	-0.9166890339	-1.1972984260	-0.9404247347
B_3	-1.85961636	-0.119874864	-1.39552718	-0.890095850
<i>Critical parameters</i>				
	R125		R600	
T_c / K	339.17		425.13	
P_c / kPa	3617.7		3796.0	

The thermodynamic conditions for the VLLE are defined by the fundamental relation:

$$f_i^{L1} = f_i^{L2} = f_i^V \quad (9)$$

i.e. the fugacities of each component in each phase are equal.

Correlating the LLE data, we found that for a quite wide range of the α value it is possible to find pairs of g_{ij} values for which:

$$Q_L = (f_i^{L_1} - f_i^{L_2})^2 < 10^{-18}$$

However, the found set of parameters did not fulfil the other conditions:

$$Q_V = (f_i^{L_1} - f_i^V)^2 + (f_i^{L_2} - f_i^V)^2 < 10^{-14}$$

which roughly corresponds to the constrains of the material balance:

$$Q_y = 1 - (y_1 + y_2) < 10^{-7}$$

For a given pressure, the thermodynamic equilibrium conditions:

$$Q_{tot} = Q_L + Q_V < 10^{-14}$$

could be found involving an additional adjustable parameter chosen between temperature, pressure, α , or x^{L_2} . Here, the α parameter was chosen. To ensure the convergence at the assumed conditions, the α parameter should be fitted to about 6-7 digits in our experimental temperature range. Considering, for example, the experimental point at $x_{R125}^{L_1} = 0.2381$, the dependence of the convergence on the α value is shown in Figure 2.

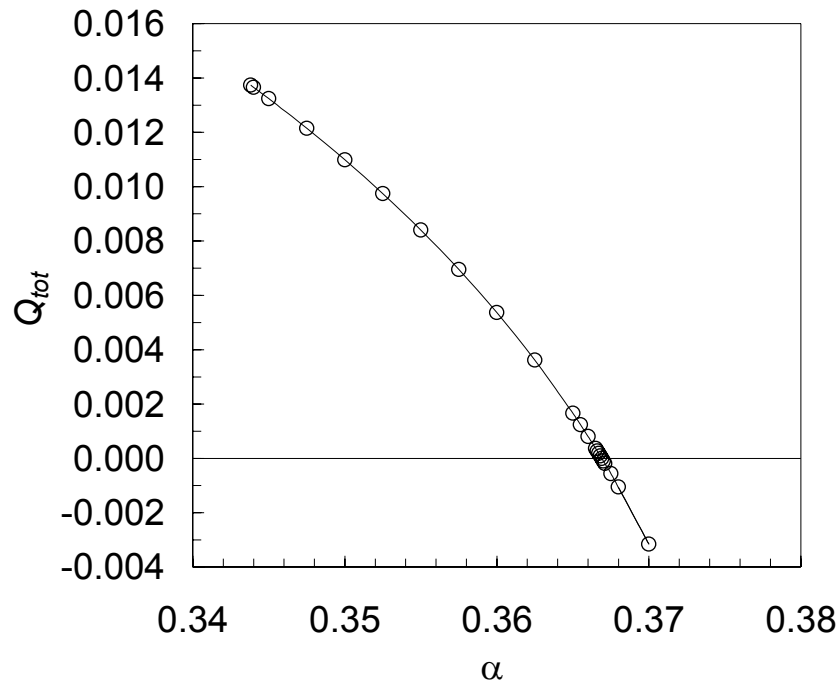


Figure 2. Dependence of the convergence of the PR EoS on the α parameter for the point $x_{R125}^{L_1} = 0.2381$, $x_{R125}^{L_2} = 0.7972$ (calculated with the polynomial), $T = 210.84$ K and $P = 47.90$ kPa.

Another possibility to reach the expected convergence is taking the pressure as the dependent variable. Considering, for example, the experimental point at $x_{R125}^{L_1} = 0.1556$, the course of the convergence is shown in Figure 3. To get the expected convergence, the pressure should be fitted to about 10^{-4} Pa! A very small shift in pressure can change

the value of the convergence. Thus it is evident how carefully both the experiment and the correlation have to be carried out to derive the VLLE parameters describing the equilibrium properties consistently.

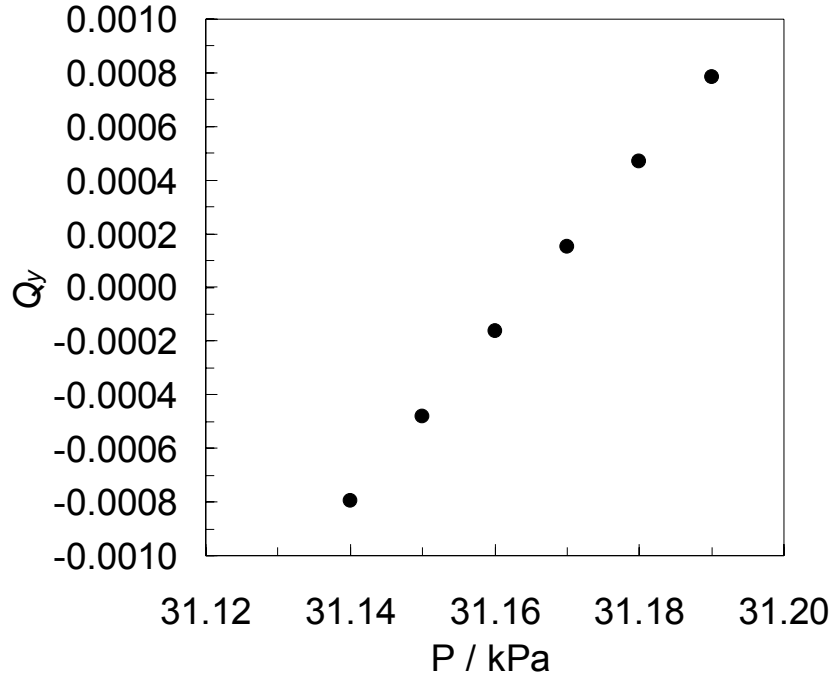


Figure 3. Dependence of the convergence of the PR EoS on pressure for $x_{R125}^{L1} = 0.1556$, $x_{R125}^{L2} = 0.8655$ (LLE from polynomial), $T = 203.79$ K and $P = 31.16$ kPa.

The results of the correlation are presented in Tables 3 and 4, and in Figures 4 and 5 for the RKS and the PR EoS, respectively. It is evident that the α and g_{ij} parameters of the NRTL equation, regressed for each point, don't show any trend with the temperature. In particular, the α value seems to be very scatter around an average value, represented by a line in the two figures. The average α values ($\alpha = 0.36713$ for RKS and $\alpha = 0.36707$ for PR EoS) are clearly different from the frequently postulated constant value $\alpha = 0.3$. The calculated composition of the vapour phase shows a slight trend with temperature, as shown in Figure 6 and lies outside of the binodal boundary. It means that the system forms an heteroazeotrope outside the two-liquid phase compositions. To identify the VLLE properties of the system, the VLE were calculated for the homogenous liquid phase using the found parameters. Over the temperature range of the experimental binodal boundary, we detected a maximum on the system pressures at vapour phase composition ($y_1 = 0.94$) that were taken as corresponding to the azeotrope. Thus, the system forms hetero-homoazeotrope at $T < T_{UCST}$. Similar results were obtained with the two equations of state and for the three different sets of the LLE data. When the temperature raises above the UCST, the system passes from homoazeotrope to zoetrope. This is clearly evident from our VLE measurements [10], performed at temperatures above 278 K. Since the results of the regression of the three sets of the LLE data are very similar, only those connected to the data calculated with the polynomial method are shown here due to space limitation.

Table 3. Results of the VLLE correlation with the RKS EoS for the R125 + R600 system. The second liquid phase composition has been derived with the polynomial method.

Sample*	α	Δg_{12} / J/mol	Δg_{21} / J/mol	$y_{R125, cal}$
1	0.38303	5145.190	4653.513	0.9226
2	0.35000	4130.128	3603.691	0.9228
3	0.36794	4370.279	3827.285	0.9191
4	0.37756	4773.547	4242.435	0.9171
5	0.36691	4274.913	3682.093	0.9165
6	0.37446	4548.067	3982.274	0.9150
7	0.37454	4547.703	3976.442	0.9142
8	0.34370	3724.313	3180.181	0.9135
9	0.37523	4719.869	4108.472	0.9119
10	0.37369	4428.784	3830.466	0.9112
18	0.36675	4005.583	3458.388	0.9109
20	0.36948	4174.944	3618.004	0.9117
21	0.34720	3774.848	3180.791	0.9134
22	0.37747	4951.994	4375.679	0.9143
23	0.35516	4031.574	3507.175	0.9176
24	0.37097	4491.984	3962.600	0.9201

*Samples are numbered as in Table 1.

Table 4. Results of the VLLE correlation with the PR EoS for the R125 + R600 system. The second liquid phase composition has been derived with the polynomial method.

Sample*	α	Δg_{12} / J/mol	Δg_{21} / J/mol	$y_{R125, cal}$
1	0.38295	5132.646	4641.334	0.9225
2	0.34920	4118.473	3591.393	0.9228
3	0.36781	4365.970	3823.216	0.9190
4	0.37755	4770.818	4240.322	0.9170
5	0.36690	4273.787	3681.370	0.9164
6	0.37448	4547.808	3982.537	0.9149
7	0.37456	4547.447	3976.721	0.9142
8	0.34380	3725.034	3181.384	0.9134
9	0.37525	4720.938	4109.992	0.9118
10	0.37371	4429.012	3831.227	0.9112
18	0.36681	4006.700	3459.892	0.9109
20	0.36953	4175.961	3619.437	0.9117
21	0.34728	3775.354	3181.812	0.9133
22	0.37748	4949.915	4374.217	0.9143
23	0.35505	4029.080	3505.000	0.9176
24	0.37079	4485.603	3956.399	0.9201

*Samples are numbered as in Table 1.

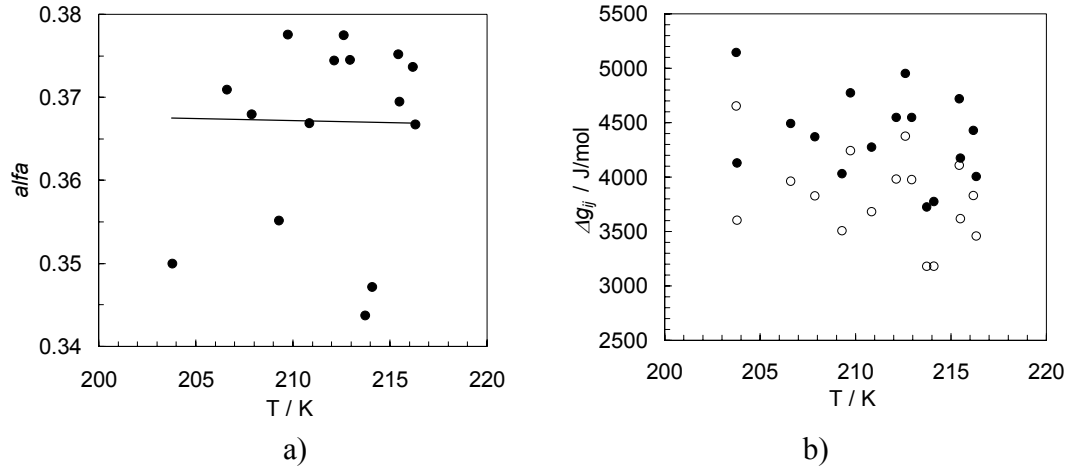


Figure 4. Coefficients resulting from the correlation with the RKS EoS: a) α vs. T , b) Δg_{12} and Δg_{21} vs. T .

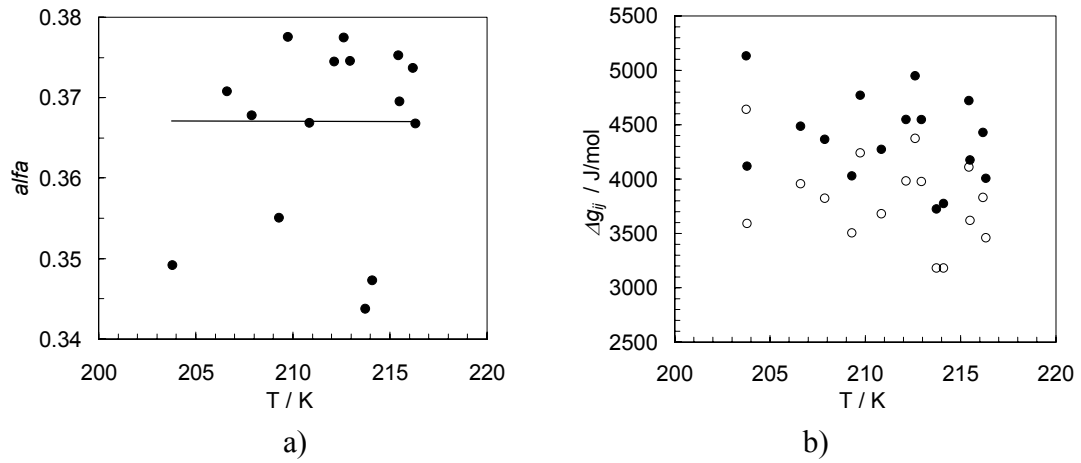


Figure 5. Coefficients resulting from the correlation with the PR EoS: a) α vs. T , b) Δg_{12} and Δg_{21} vs. T .

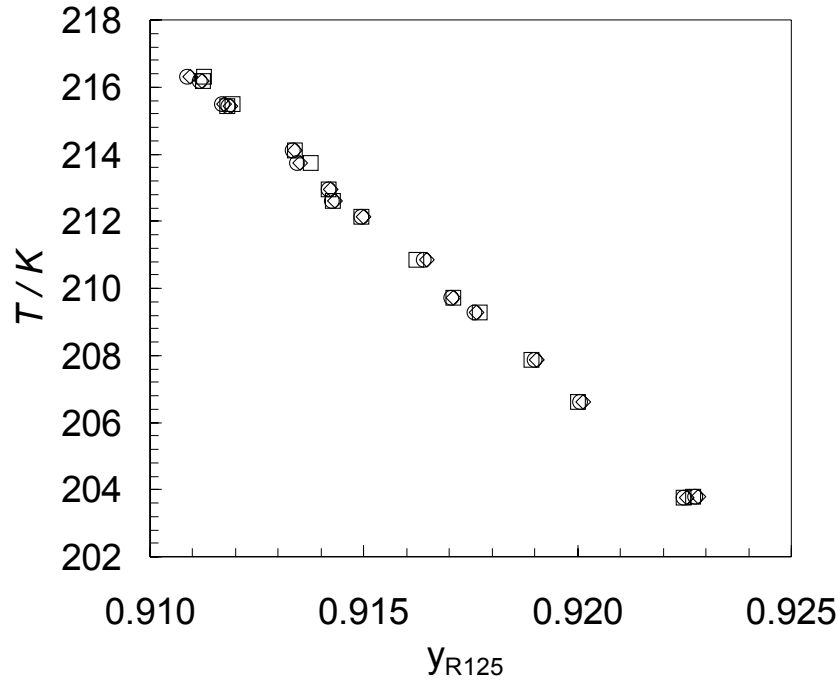


Figure 6. Calculated vapour phase compositions: (\diamond) - RKS EoS, LLE from polynomial, (\circ) - PR EoS, LLE from polynomial, and (\square) – from equation 3.

4. Conclusions

The method used to correlate solubility data (if they represent both branches of the binodal boundary) through EoS, involving the $x_{est}^{L_2}$ value in addition to the measured T , P and $x_{exp}^{L_1}$ values, proved successful. Numerically, the models can be applied up to temperatures close to the UCST, but with increasing difficulty the closer it comes to the UCST. The methods to estimate the second liquid phase composition coexisting in equilibrium may be quite accurate and all the three applied methods lead to consistent results. Within the temperature range of the experiment, the system forms hetero-homoazeotrope. Moreover, the regression of the experimental P - T sequences, even if the composition is not explicitly involved, can be used as an auxiliary tool to detect crude experimental errors. Negligible differences between the results obtained from the RKS and the PR EoS were found.

List of symbols

f = fugacity

P = pressure (kPa)

T = temperature (K)

x = liquid mole fraction

y = vapour mole fractions

Greek letters

Φ = fugacity coefficient

Subscripts

1, 2 = one fluid phase

c = critical

est = estimated

exp = experimental

i, j = one component of the mixture

Superscripts

L = liquid phase

V = vapour phase

Acknowledgments

Roman Stryjek is indebted to CNR-ITC in Padova for the financial support during his visit.

References

- [1] S. Bobbo, L. Fedele, R. Camporese, M. Scattolini and R. Stryjek, Fluid Phase Equil., in press.
- [2] S. Bobbo, L. Fedele, R. Camporese and R. Stryjek, Fluid Phase Equil., in press.
- [3] R. Stryjek and M. Rogalski, Bull. Ac. Pol. Chim., 28 (1980), 139-147.
- [4] G. Soave, Chem. Eng. Sci., 27 (1972) 1197-1203.
- [5] D. Y. Peng and D. B. Robinson, Ind. Eng. Chem. Fundam., 15 (1976) 59-64.
- [6] M. S. Zabaloy and J. H. Vera, Ind. Eng. Chem. Res., 37 (1998), 1591-1597.
- [7] E. W. Lemmon, M. O. McLinden, M. L. Huber, Reference Fluid Thermodynamic and Transport Properties (REFPROP), Version 7.0 (Gaithersburg: NIST, 2002).
- [8] M. J. Huron and J. Vidal, Fluid Phase Equil., 3 (1979) 255-272.
- [9] H. Renon and J. M. Prausnitz, AIChE J., 14 (1968) 135-144.
- [10] L. Fedele, S. Bobbo, R. Camporese and R. Stryjek, in preparation.